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13. ABSTRACT (Maximum 200 words) Elemental parameter sets have been completely developed and validated for sulfur (S), silicon (Si), and phosphorous (P). Extensive work has been completed on SAM1 parameters for iron (Fe), although final results are not available. Substantial obstacles have been overcome in the iron work and a clear route to the objective has been established. The theoretical framework is in place and all that is required is completion of the parameterization process. The experience we have gained will allow us to parameterize SAM1 for other transition metals very quickly. The primary question of this research as to whether the Dewar-style semiempirical methodology could be extended to transition metals has been answered in the very definite affirmative. Dr. George Famini, the technical officer for the project, suggested that we suspend work on arsenic (As) and copper (Cu) in favor of iron, a request with which we complied.			
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Proposed Objectives of the Research

The objective of the proposed research was to expand a new semiempirical method, SAM1, that explicitly includes treatment of *d*-orbitals. The elements for which parameters were to have been developed are sulfur (S), silicon (Si), phosphorous (P), arsenic (As), and copper (Cu).

Attained Objectives of the Research

Elemental parameter sets have been completely developed and validated for sulfur (S), silicon (Si), and phosphorous (P). Extensive work has been completed on SAM1 parameters for iron (Fe), although final results are not available. Dr. George Famini, the technical officer for the project, suggested that we suspend work on arsenic (As) and copper (Cu) in favor of iron, a request with which we complied.

Statement of Work Completed

1. Molecular Basis Set for Parameterization (MBSP) updated and expanded for silicon.
2. MBSP updated and expanded for sulfur.
3. MBSP updated and expanded for phosphorous.
4. MBSP created for iron.
5. MBSP created for copper.
6. SAM1 parameters completed for silicon.
7. SAM1 parameters completed for sulfur.
8. SAM1 parameters completed for phosphorous.
9. Recoding of AMPAC and the parameterization program to allow full and correct communication and interchange of data between the two modules.
10. Exploration of multiplicity and electronic state problems surrounding the description of the iron systems in the MBSP.
11. Derivation of a stable and predictable Configuration Interaction (CI) process for use in the parameterization.
12. Preliminary grid searches completed for one-center/one-electron integrals for iron.
13. Preparation of data and presentation of results at the American Chemical Society National Meeting in San Diego.

Results and Discussion

As noted in Appendices 1, 2, and 3. Highly successful SAM1 parameters for silicon, sulfur and phosphorous have been completed. The results show a substantial improvement over preceding generations of semiempirical methods, especially for hypervalent systems. The *d*-orbitals included with SAM1 have made an important difference in this context. This

advance is a substantial addition to the capabilities of computational chemists, allowing them to study many industrially important processes that have previously been treatable only by high level *ab initio* approaches.

Appendix 4 lists preliminary results for iron within the SAM1 protocol. As is readily evident, these results are not up to the par expected for methods of this complexity and is certainly not in keeping with historical performance. As noted, however, these results are preliminary. They are presented in this context to illustrate that the method is a *viable approach* to the problem of modeling transition metals with semiempirical methodology. It should be emphasized at the outset of this discussion that the work on iron and other transition metals is a completely new area using Dewar-style semiempirical theory. Previous experience has largely been with closed-shell systems (singlet spin state) and with much more "regular" chemistry. This is certainly not the case with transition metals. Semiempirical methods found their first real application in the context of organic molecules and reactions and have only recently moved to heavier main group elements.

The results presented here for iron are for a very simplistic closed-shell, restricted Hartree-Fock treatment of the wavefunction. We began with this approach (which we certainly do not intend to finish the project using) as a way of exploring the problems that will be encountered in the parameterization of elements with high spin states requiring extensive use of Configuration Interaction (CI). In this light, our efforts have been very instructive and valuable. A number of obstacles have been identified and most have already been overcome. Some of these are listed below. An asterisk (*) indicates that we have solved the problem and are moving forward.

- re-coding of AMPAC to handle very large open-shell multiplicities such as are routinely encountered with transition metals *
- development of new CI algorithms and approaches *
- errors in the structure of the parameterization program that led to incorrect passing of data between it and AMPAC when CI was invoked *
- difficulty extrapolating initial values for the parameters from which to begin searches *
- energy separation of the parameters describing the one-electron/one-center energies
- ordering of the atomic orbital levels
- partially automated approach to CI for easier calculation and determination of the minimum level of CI required for a particular system

- lack of high quality experimental data on spin multiplicity *

The implementation of "automatic CI" will be an important consideration in future work with transition metal systems. Calculations on organic systems require CI to be used only in very special circumstances, whereas it will need to be applied almost routinely with transition metals. We intend to add a set of program code that will predict which MO's occupied by which electrons need to be mixed and automatically provide that pattern using various AMPAC options (the OPEN keyword). (The user will obviously be able to override these default values if the need arises.) At present, we intend to use the "natural" first guess from AMPAC to commence the SCF procedure for automatically assigning the CI mixing pattern. In this approach, the RHF wavefunction from which the microstates are constructed for subsequent mixing is one where orbital occupancy and degeneracy patterns are well-defined. Open-shell systems are treated in this context using the half-electron (more aptly named the "partial electron") approximation pioneered by Dewar and coworkers.

There is a problem with this from the parameterization standpoint in that the natural pattern first generated is almost exclusively dependent on the U_{ss} , U_{pp} , and U_{dd} parameters. This means that the "correct answer" in terms of orbital degeneracy and ordering must be an *input* to the parameterization run rather than a result. We plan to overcome this limitation by applying either *ab initio* or density functional methods to the MBSP systems and using these results to input the correct level and type of CI required for the system.

Conclusions

In summary, the work proposed was carried out with a large degree of success. Excellent new parameters have been developed for treating Si, S, and P. While the research leading to SAM1 parameters on iron are not complete, this is only a matter of time at this point. Substantial obstacles have been overcome and a clear route to the objective has been established. The theoretical framework is in place and all that is required is completion of the parameterization process. The rate at which such pioneering work could be carried out was perhaps over-estimated in our initial proposal, but iron should be finished very soon. The experience we have gained will allow us to parameterize SAM1 for other transition metals very quickly. The primary question of this research as to whether the Dewar-style semiempirical methodology could be extended to transition metals has been answered in the very definite affirmative.

Appendix 1: SAM1 Results for Silicon

Property	# Species	SAM1	Error AM1	PM3
ΔH_f (kcal)	62	6.09	7.33	6.56
μ (D)	20	0.36	0.41	0.75
IP (eV)	43	0.54	0.58	0.77

Appendix 2: SAM1 Results for Phosphorous

Property	# Species	SAM1	Error AM1	PM3
ΔH_f (kcal)	60	9.97	16.63	15.82
μ (D)	17	0.66	0.99	1.02
IP (eV)	38	0.69	0.84	0.93

Appendix 3: SAM1 Results for Sulfur

Property	# Species	SAM1	Error AM1	PM3
ΔH_f (kcal)	76	6.45	7.09	9.33
μ (D)	45	0.40	0.49	0.59
IP (eV)	67	0.39	0.33	0.39

Appendix 4: Preliminary SAM1 Results for Iron

Molecule	ΔH_f	Error in:	
		Ioniz. Pot.	Dipole Moment
FeH	-3.1 ¹	-5.5 ²	3
FeBr ₂	43.4	-	-
FeBr ₃	63.0	-	-
Fe ₂ Cl ₄	10.4	-5.7	-
Fe ₂ I ₄	16.6	-	-
FeCl ₂	3.2	-6.1	-
FeCl ₃	-16.2	-	-
Fe(CO) ₄	5.2	-2.7	-
Fe(CO) ₅	-4.9	-0.2	-
Ferrocene	-50.1	2.2	-
FeCH ₃	9.4	-	-
FeOH	-12.3	-6.3	-
Fe(OH) ₂	34.6	-	-
Average (MU)	30.5	1.06	4.89
# Molecules	26	15	2

1. kcal/mol. 2. eV. 3. Debyes.